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This report gives the details of the analytical procedures that must be used to control the quality of Neoprene 5109S and of Nitrile BLT2. Also given are the concentrations of the fomulation ingredients that must be achieved in order for the rubber batch to be qualified for application in sonar transducers.

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Compositional Analysis Procedures for Selected Elastomers Used In Sonar Transducers

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COMPOSITIONAL ANALYSIS PROCEDURES FOR SELECTED ELASTOMERS USED IN SONAR TRANSDUCER

INTRODUCTION

The quality control of elastomers has been attempted for many years by the use of a battery of physical tests. There are several severe problems with this approach. First is that the properties chosen for the requirements list must reflect the real engineering requirements. The problem with this approach is that the engineering requirements imposed on the elastomer are frequently not well understood. Many times the designers seem to treat the rubber as something that is so simple that it will perform any task they choose without regard to the foibles of rubber science and engineering. A common example for underwater transducers is when inadequate attention is paid to the method of sealing water from the transducer. It has happened that a rubber with poor creep properties is clamped or banded into place, with almost inevitable leaking later in the life cycle. On the other hand, if the engineering requirements are carefully considered and tests exist that can reasonably be used to determine if a given batch of rubber meets these requirements, then this approach will work. The reality is that this is usually just not done.

The realization that rubber quality control cannot be left to the design engineers has caused us to take an alternative, but not necessarily innovative, approach. This approach is given in the following steps: (1) a rubber formulation is optimized for a given application; (2) that formulation is specifically called for; and (3) tests are devised that can assure that that formulation is indeed supplied. This report will give the procedures that have been developed to assure the composition of samples of two Navy formulations developed for underwater acoustical applications.

QUALITY CONTROL SCHEME

Samples of uncured rubber are taken from at least three positions within each batch of rubber furnished for transducer manufacture. A portion of each of these is cut into small pieces, dissolved, filtered, and subjected to chromatographic analysis. The undissolved residue gives an estimate of the carbon black; the chromatographic analysis gives the concentrations of the organic additives and the metal oxide; and if desired, gel permeation chromatography applied to the filtrate will show the molecular weight distribution of the polymer. The statistical dispersion of the results for the multiple sampling sites within each batch is a measure of the homogeneity of the batch. Wet chemistry or spectroscopy may also be applied to the solution of the polymer to determine other quality factors.

It has been a driving requirement in the development of our compositional analysis quality control scheme that the composition results obtained must not stand alone. They have in every case been linked to a significant physical property. That is to say, no composition factors are specified that do not have an impact on the properties of the resulting cured rubber. This linking

has been done in this research by means of our so-called off-specification test. In this test, samples of the formulation are acquired that contain purposely introduced variations in composition. These samples are analyzed and subjected to a thorough battery of physical property tests. The compositional analysis results are then correlated with the physical property data to yield the desired linking. Frequently, the correlation is obvious. For example, when the level of antioxidant is low, the oxidation resistance of the sample is low. However, some of the correlations are more subtle and perhaps show up only when the data are treated with computer correlation programs. The required compositional levels for each of the different rubber types are determined after careful consideration of each physical property requirement and the compositional variables that drive that physical property.

There is at least one case where the compositional analysis is not sufficiently accurate to adequately predict an important physical property. This is the carbon black analysis where results are contaminated by the almost inevitable undissolved polymer residue. Consequently, a check on this analysis is usually done by measuring the volume electrical resistivity of a cured sample of the rubber. Shore A hardness or density may also be useful measures of carbon black content.

NEOPRENE 5109 SERIES

A formulation similar to Neoprene 5109 was originally developed as the environmental protection layer for special hull treatment tiles. NRL Memorandum Report No. 5818 * describes how this formulation was optimized for use in sonar transducers. Neoprene 5109 and the softer version, 5109S, are intended for use where the principal engineering requirement is bondability. This is typically the case where a vulcanizing bond forms the primary seal against water ingression. In addition to superior bondability, the Neoprene 5109S has the properties of good strength, good environmental resistance, moderate dynamic losses, good electrical properties, and fair-to-poor compression set resistance.

Neoprene 5109S has the following formulation:

Neoprene GRT polymer	100	parts by weight
Stearic Acid cure activator	2	parts by weight
Benzothiazyl Disulfide (MBTS) cure retarder	1.5	parts by weight
Octamine (ODPA) antioxidant	2	parts by weight
Pb_3O_4 dispersion cure agent	15	parts by weight
TE-70 proprietary process aid	2	parts by weight
N550 carbon black	31	parts by weight

With 40 parts of the N550 carbon black, the formulation is called Neoprene 5109; with 25 parts, it is called Neoprene 5109SS.

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*C.M. Thompson and L.L. Beumel, "A Neoprene with Optimized Bondability for Sonar Transducer Applications," NRL Memorandum Report 5818 (1986).

Neoprene 5109 Analytical Procedures

Samples of the Neoprene 5109 type of rubber are analyzed by a combination of wet chemistry, reverse-phase liquid chromatography, and complexation chromatography. The details of these analyses are given in Appendix A.

Neoprene 5109 Requirements

In order to meet the requirements of Naval Sea Systems Command (NAVSEA) Drawing No. 53711-5516934, the analyzed compositional levels for Neoprene 5109S shall be as follows:

MBTS Residue	0.07-0.18% by weight*
ODPA Concentration	0.8-2.0% by weight
Pb_3O_4 Concentration	7.5-9.5% by weight
Carbon Black Concentration	30-45% by weight.**

In addition to these compound concentrations, it is also important to judge whether there are any unexpected peaks in the chromatogram that might indicate extraneous additives in the rubber. This is somewhat subjective as there are many peaks that regularly appear in the chromatogram that probably result from the various fragmentation products of the MBTS and the stabilizer that is included by the polymer manufacturer. Of particular interest would be any peaks that occur later in the chromatogram as these may be indicative of an undesirable oil or plasticizer in the formulation. The presence of any such extraneous peaks should alert the chromatographer to the possibility of prohibited additives.

NITRILE BLT2 COMPOUND

Nitrile BLT2 was designed for specific use as a damper in the tail mass assembly of the TR-317R sonar transducer. The formulation is similar to that of Nitrile 6100, which has been used in other dynamic absorbing applications. The procedures and permitted concentrations given here may also be used for Nitrile 6100 with only minor modifications.

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* MBTS is a reactive component during the rubber mixing. The required level really means that there must be some MBTS remaining in the mixed rubber, but not so much as to precipitate and cause bonding problems.

** For 5109S, a range of 35 to 50% is suitable for 5109. Carbon black concentrations are quite subjective. If a sample falls outside of these ranges, it should not be rejected without confirmatory evidence. This evidence is a log volume electrical resistivity that falls outside of the range of 9.5 and 10.5 for the 5109S or 9.0 and 10.0 for 5109. A Shore A hardness that falls outside of the range of 55 to 65 (5109S) may indicate too little or too much carbon black, but there are other compositional factors that can cause such a variation. Consequently, Shore hardness provides only a weak confirmation of a suspected problem with carbon black analysis.

Nitrile BLT2 has the following formulation:

Paracril BLT	100	parts by weight
Stearic Acid cure activator	1	parts by weight
ODPA antioxidant	2	parts by weight
Tetramethyl Thiuram Monosulfide (TMTM) cure accelerator	0.5	parts by weight
Sulfur cure agent	1.5	parts by weight
Zinc Oxide cure activator	5	parts by weight
N550 carbon black filler	40	parts by weight.

Since this material is intended for a dynamic application, the acrylonitrile content of the acrylonitrile-butadiene copolymer is one of the most important compositional variables. The Paracril BLT polymer was chosen because the manufacturer (Uniroyal) has been the most receptive to permitting tight control of their acylonitrile content. The TR-317R transducer functions best when the acrylonitrile content of the polymer is near 31.5%. A variation of ±1.4% has been called for in the specification.

Nitrile BLT2 Analytical Procedures

The Nitrile BLT2 is analyzed by a combination of wet chemistry, reverse-phase liquid chromatography, and complexation chromatography. The details of these procedures are given in Appendix B.

Nitrile BLT2 Requirements

To meet the requirements of NAVSEA Drawing No. 53711-5516954, the analyzed composition of the sample must be as follows:

TMTM Concentration	0.25-0.40% by weight*
ODPA Concentration	0.8-2.0% by weight
Zinc Oxide concentration	1.5-3.5% by weight
Sulfur Concentration	0.7-1.2% by weight
Carbon black concentration	25-45% by weight**
Acrylonitrile (in polymer)	31.1-33.9% by weight

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* TMTM is partially consumed in the mixing process and the level given here represents how much residue should remain in the mixed rubber. Empirical means of indicating the TMTM concentration, such as rheometer testing, have been investigated and were not found to be sufficiently accurate for Nitrile BLT2 quality control.

** Carbon black concentrations as measured here are not as significant a quality control tool as is a measure of the sample modulus. Consequently, samples should not be rejected based solely upon the carbon black concentration. Shore A hardness testing, as defined within NAVSEA Drawing No. 53711-5516954, is a simpler and more direct predictor of the rubber modulus and the impact this has upon the performance of the sonar transducer.

Appendix A

NEOPRENE 5109 ANALYTICAL PROCEDURES

INTRODUCTION

This section gives details of the quality control procedures developed for analyzing the additives in an uncured, compounded neoprene rubber. Reverse-phase high-performance liquid chromatography (HPLC) measures the levels of benzothiazyl disulfide (MBTS) and octamine (ODPA). The lead oxide content is measured by using complexation chromatography, and an estimation of carbon black content is determined gravimetrically.

SAMPLE PREPARATION

1. Samples of uncured, compounded Neoprene GRT are stored in a 0°F freezer until analyzed.

2. Approximately 50 mg of rubber are cut from each sampling site on the frozen slab of rubber and diced into small (1 mm^3) pieces.

3. The diced rubber is placed in a desiccator for about 30 minutes to allow the rubber to come to room temperature and remove any absorbed moisture.

4. A 25 ±2-mg portion of the diced rubber is weighed to the nearest 0.01 mg on a microbalance and placed in a threaded test tube containing 6 ml of UV-grade tetrahydrofuran (THF). The tube is tightly sealed with a screw cap and gently agitated/rotated until the rubber has dissolved (about 30 minutes, depending upon the condition and state of cure of the elastomer).

5. The dissolved rubber sample is filtered into a 10.00-ml volumetric flask using a Millipore 47-mm stainless-steel filter and a dried, pre-weighed Rainin filter, 0.45-μm pore size. Prior to use, each filter is brought to constant weight by heating in an oven at 100°C for about one hour. After cooling, each filter is weighed to the nearest 0.01 mg on a microbalance and stored in a desiccator.

6. The solution in the volumetric flask is adjusted to 10.00 ml with UV-grade THF. The THF solution is now ready for liquid chromatography (LC) additive analysis. The residue on the nylon filter contains red lead, carbon black, and debris that have entered the sample during the compounding process. Additional processing of the residue on the filter is necessary to measure the carbon black and red lead levels.

7. Uncured, compounded samples of neoprene will begin to cure at room temperature. Mistreatment will result in a partially cured sample. An analysis of partially cured samples will produce poor data. Partially cured samples of neoprene will not disperse completely in THF. When filtered (step 5, above), small, irregularly shaped pieces of undissolved rubber will be found on the filter. In contrast, when an uncured sample is filtered, a smooth, even, velvet-like layer of carbon black and red lead is deposited on the filter. Suspect samples should be checked (prepare a new sample and attempt to disperse in THF) before proceeding with the HPLC analyses.

A regression equation describing the response of the detector over the concentration range of the calibration standards can also be calculated from the calibration data. The regression equation should be checked on a daily basis as described above. Calculation of a regression equation should not be used as a substitute for drawing a calibration curve.

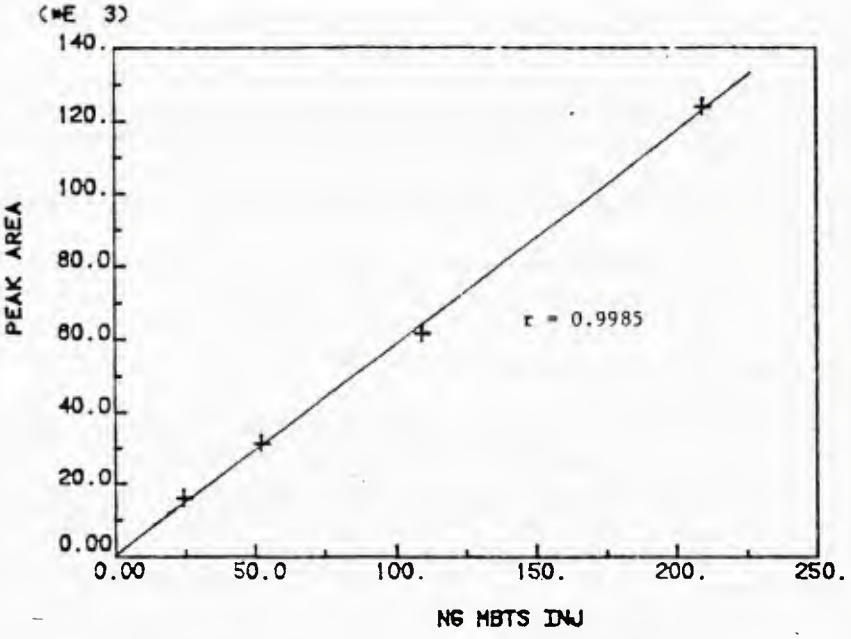

Fig. A1 - Calibration curve for MBTS

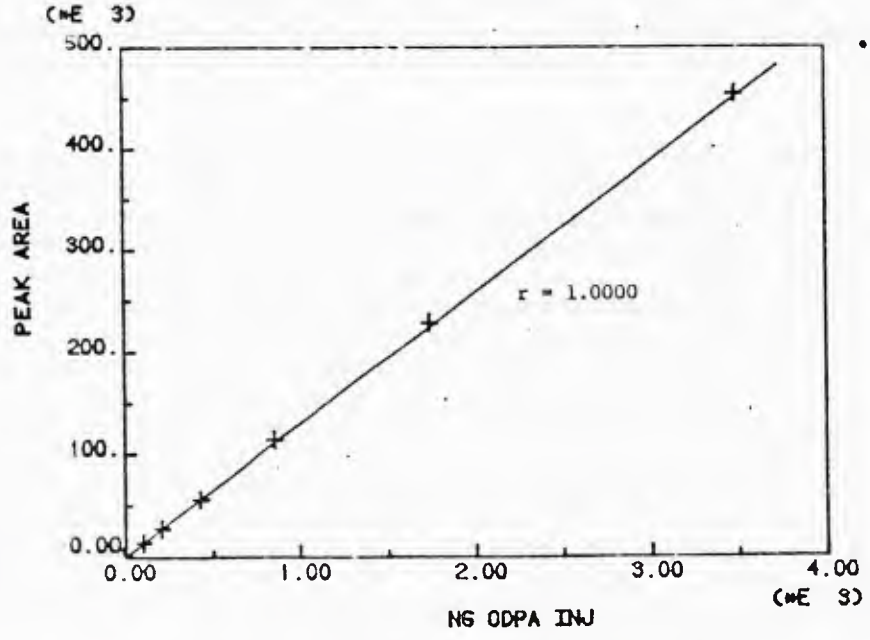

Fig. A2 - Calibration curve for ODPA

3. Chromatographing Mixed Standards and Rubber Solutions

NOTE: The procedure for generating the additive chromatograms will depend upon the LC equipment and data reduction facilities available. The procedure described below is for a automated LC system under computer control.

a. Optimum operating conditions are established on the LC by using the operating parameters listed in the previous section.

b. The autosampler vials are filled with the THF solutions of mixed standards and the dissolved, filtered rubber sample solutions.

c. A 10-μl portion of each solution is injected onto the column. At least three injections of each solution are chromatographed. Both MBTS and ODPA are monitored in each injection. Wash vials containing THF are placed between standard and sample vials (on the autosampler) to avoid cross contamination between solutions. Representative chromatograms of a mixed standard solution and rubber solution are shown in Fig. A3.

d. When all of the standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to additive percentages.

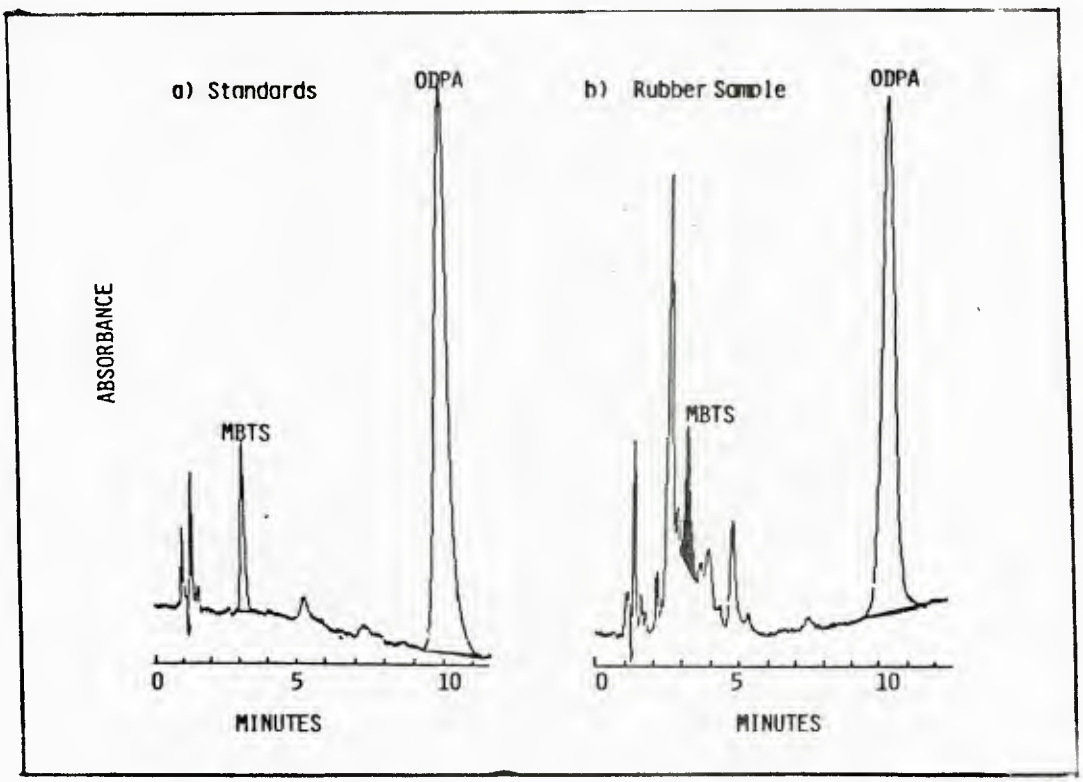

Fig. A3 - LC chromatograms of a mixed standard solution and a neoprene rubber sample

4. Data Reduction

The percentage of organic additive in the rubber sample can be calculated using the following equation:

$$\% \text{ Additive} = \frac{\text{mg of additive present in the rubber sample}}{\text{sample weight, mg}} \times 100 \; . \qquad \text{(A1)}$$

Sample weight is the weight of the rubber sample in milligrams initially dissolved in THF. Weight of the additive in milligrams present in the rubber sample can be calculated using the following equation:

$$\text{Wt. of Additive in Sample, mg} = \text{Wt. of Additive in Injection, ng} \times \frac{\text{Dilution Volume (ml)}}{\text{Injection Volume } (\mu\text{l})} \times \frac{10^3 \, \mu\text{l}}{1 \text{ ml}} \times \frac{1 \text{ mg}}{10^6 \text{ ng}} . \qquad \text{(A2)}$$

Weight of the additive in the injection in nanograms can be determined using the measured peak area and the calibration curve (as shown in Figs. A1 and A2) or from the regression equation describing the calibration curve. It is important that the calibration curve be prepared and that the linearity of the relationship between weight of additive and peak area be checked before generating and using the regression equation. The weight of additive in the injection in nanograms can be calculated from the regression equation using the following equation:

$$\text{Wt. of Additive in Injection, ng} = \text{Slope of Regression Line} \times \text{Area Under Sample Curve} + \text{Intercept of Regression Line} \; . \qquad \text{(A3)}$$

Sample Calculation:

Figure A3b, a chromatogram of a neoprene sample, shows how the area under the MBTS peak is determined by interpolating the baseline between the start and finish of the peak, since the peak is not completely resolved. The area of the peak was determined to be 15202 by computer software. From the calibration curve for MBTS (Fig. A1), a peak area of 15202 corresponds to approximately 26 ng of MBTS injected. Weight of MBTS calculated from the calibration curve (26 ng) is inserted into Eq. (A2) to calculate the weight of the additive (in mg) in the sample. The percentage of MBTS is calculated by inserting the weight of MBTS in the sample into Eq. (A1).

$$\text{Wt. of Additive in Sample, mg} = 26 \text{ ng} \times \frac{10.00 \text{ ml}}{10.0 \; \mu\text{l}} \times \frac{10^3 \, \mu\text{l}}{1 \text{ ml}} \times \frac{1 \text{ mg}}{10^6 \text{ ng}} \; , \qquad \text{(A4)}$$

where 10.0 μl is the size of the injection used for this example and 10.00 ml is the volume into which the rubber sample is dissolved,

$$\% \text{ Additive} = \frac{0.026 \text{ mg}}{25.00 \text{ mg}} = 0.103\% \ , \tag{A5}$$

where 25.00 mg is the weight of the rubber sample initially dissolved in THF.

If the regression equation for the calibration curve has been calculated, the weight of MBTS in the injection can be calculated by inserting the peak area (15202) into Eq. (A3). The weight of MBTS in the sample can be calculated by inserting the weight of MBTS in the injection into Eq. (A2). The percentage of MBTS is calculated by inserting the weight of the MBTS in the sample into Eq. (A1).

$$\begin{aligned} \text{Wt. of Additive in Injection} &= 1.7105\text{E-}03 \times 15202 + (-3.2612\text{E-}01) \\ &= 25.68 \text{ ng MBTS}, \end{aligned} \tag{A6}$$

$$\begin{aligned} \text{Wt. of Additive in Sample} &= 25.68 \text{ ng} \times \frac{10 \text{ ml}}{10 \ \mu\text{l}} \times \frac{10^3 \ \mu\text{l}}{1 \text{ ml}} \times \frac{1 \text{ mg}}{10^6 \text{ ng}} \\ &= 0.02568 \text{ mg MBTS}, \end{aligned} \tag{A7}$$

$$\% \text{ Additive} = \frac{0.0256 \text{ mg}}{25.00 \text{ mg}} \times 100 = 0.103 \ \% \text{ MBTS}. \tag{A8}$$

LIQUID CHROMATOGRAPHY ANALYSIS OF LEAD OXIDE (Pb_3O_4)

1. Optimized Operational Parameters

   Column: Waters μBondaPAK C_{18}, 30 cm

   Injection Size: 100-μl loop

   Analysis Wavelength: 545 nm; Sensitivity = 0.05 or 0.10 AUFS

   Mobile Phase: 70% Acetonitrile/30% Acetate Buffer pH 4.6/1.5 E-04M dithizone (procedure for preparation is given below).

   Preparation of Acetate Buffer: 16.4-g anhydrous sodium acetate (27.2-g sodium acetate trihydrate), and 10.00-ml glacial acetic acid diluted to 1000.00 ml with deionized water.

   Purification of Dithizone: Dithizone is unstable and must be purified on a weekly basis. To purify, dissolve 1 g of dithizone in 50 to 75 ml of chloroform. Extract with four 100-ml portions of 0.2M NH_4OH. Filter the aqueous extracts into a separatory funnel. Acidify with 6M HCl until the solution becomes acidic to litmus paper, and extract precipitate

mixture with three 20-ml portions of $CHCl_3$. This stock solution of dithizone in chloroform should keep for several days if stored in the dark at 5 to 10°C.

Preparation of Mobile Phase: To prepare 1 liter of mobile phase, the chloroform is evaporated from several ml of the stock solution and 35 mg of dried dithizone is weighed and dissolved in 700 ml of acetonitrile. The acetate buffer is added (300 ml) and the solution filtered (0.45 μm) and degassed. The mobile phase must be prepared fresh daily.

Flow Rate: 1.0 ml/min.

Temperature: Ambient

Reactor Tubing: Reactor tubing is placed between the injector and column to assure complete metal-complex formation prior to entering the column. The reactor tubing is made by coiling 20 cm of 0.030-in. i.d. stainless steel tubing.

2. Detector Response Calibration

The UV-detector response is calibrated daily by injecting standards of varying concentration and by measuring the peak area for each injection. Concentration of Pb^{2+} standard solutions should range from 100 to 1000 ng injected. The stock solution of the standard should be prepared by accurately weighing dried $Pb(NO_3)_2$ and dissolving the $Pb(NO_3)_2$ in a suitable amount of glacial acetic acid such that the final percentage of acetic acid in the flask is 1%. For example, a stock solution containing 1-g Pb^{2+}/liter may be prepared by dissolving 0.1598 g of $Pb(NO_3)_2$ in 1 ml of glacial acetic and diluting to 100.00 ml with HPLC-grade water. Three or, preferably, four dilutions of the stock solution should be made using a 1% acetic acid solution as the diluent. A calibration curve should be prepared by plotting peak area (ordinate) vs nanograms of standard injected (abscissa). When preparing the calibration curve, special attention should be given to the high concentration portion of the calibration curve where a nonlinear response may be encountered with some HPLC systems. If a nonlinear calibration curve is encountered, standard and sample solutions must be diluted to bring the calibration range into the linear response range of the detector. At the low end of the calibration curve, the curve should intersect the axes near zero area and zero concentration. If this is not observed, it may indicate that the mobile phase had begun to decompose or that the peak detection "window" of the computer software or the peak detection sensitivity (slope sensitivity) of the integrator was not properly set to detect the peak. Figure A4 shows a typical calibration curve for lead.

A regression equation describing the response of the detector over the concentration range of the calibration standards can also be calculated from the calibration data. The regression equation should be checked on a daily basis as described above. Calculation of a regression equation should not be used as a substitute for drawing a calibration curve.

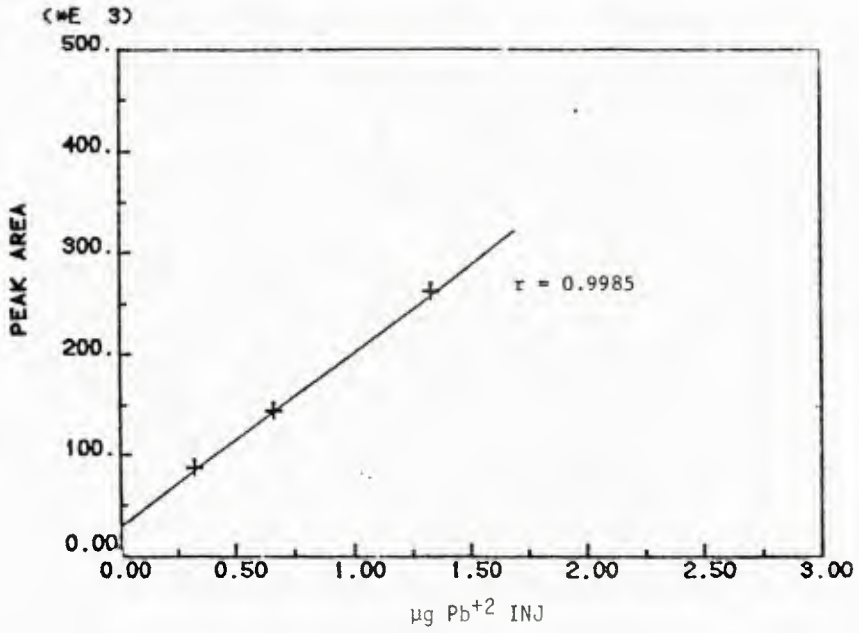

Fig. A4 - Calibration curve for Pb^{2+}

3. Chromatographing Lead Solutions

a. Optimum operating conditions are established on the LC by using the parameters in Section 1 of the Liquid Chromatography Analysis of Lead Oxide.

b. The autosampler vials are filled with the dilute acetic acid solutions of lead standards and lead recovered from rubber.

c. A 100-μl portion of each lead sample is injected. A least three injections are made on each solution. Wash vials of dilute acetic acid are placed between standard and sample vials (on the autosampler) to avoid cross contamination between samples.

d. When all standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to lead oxide percentages.

4. Data Reduction

The percentage of lead oxide in the rubber sample can be calculated using the following equation:

$$\% \, Pb_3O_4 = \frac{\text{mg of } Pb_3O_4 \text{ present in rubber sample}}{\text{sample wt., mg}} \times 100. \qquad \text{(A9)}$$

Sample weight is the weight of the rubber sample in mg initially dissolved in THF. Weight of the lead oxide in mg present in the rubber sample can be calculated using the following equations:

$$\text{Wt. of } Pb^{2+} \text{ in Sample, mg} = \text{Wt. of } Pb^{2+} \text{ in Injection, } \mu g \times \frac{\text{Dilution Volume(ml)}}{\text{Injection Volume}(\mu l)} \times \frac{10^3 \mu l}{1 \text{ ml}} \times \frac{\text{mg } Pb^{2+}}{10^3 \mu g} . \quad \text{(A10)}$$

$$\text{Wt. of } Pb_3O_4 \text{ in Sample, mg} = \text{Wt. of } Pb^{2+} \text{ in Sample, mg} \times \frac{\text{mmole } Pb^{2+}}{207.21 \text{ mg } Pb^{2+}} \times \frac{1 \text{ mmole } Pb_3O_4}{3 \text{ mmole } Pb^{2+}} \times \frac{685.63 \text{ mg } Pb_3O_4}{\text{mmole } Pb_3O_4} . \quad \text{(A11)}$$

Weight of Pb^{2+} in the injection in nanograms can be determined using the measured peak area and the calibration curve (Fig. A4). The weight of Pb^{2+} in the sample must be converted to weight of Pb_3O_4 in the sample using Eq. (A11).

A regression equation may be used to calculate the weight of Pb^{2+}; however, before using the regression equation, the calibration curve must be prepared and the linearity of the relationship between weight of additive and peak area checked. The weight of additive in the injection in nanograms can be calculated from the regression equation using the following equation:

$$\text{Wt. of } Pb^{2+} \text{ in Injection, } \mu g = \text{Slope of Regression Line} \times \text{Area Under Sample Curve} + \text{Intercept of Regression Line.} \quad \text{(A12)}$$

As before, the weight of Pb^{2+} in the sample must be converted to weight of Pb_3O_4 in the sample using Eq. (A11).

Sample Calculation:

Figure A5 shows a chromatogram of lead solution recovered from a neoprene rubber sample. The area of the peak was determined to be 157898 by computer software. From the calibration curve for Pb^{2+}, a peak area of 157898 corresponds to 0.75 μg of Pb^{2+} injected. The weight of Pb^{2+} in the sample is calculated by inserting the value into Eq. (A10). The weight of Pb_3O_4 in the sample is calculated by inserting the weight of Pb^{2+} in the sample into Eq. (A11). The percentage of Pb_3O_4 is calculated by inserting the weight of Pb_3O_4 into Eq. (A9).

$$\text{Wt. of } Pb^{2+} \text{ in Sample, mg} = 0.75\ \mu g\ Pb^{2+} \times \frac{250.00\ ml}{100.00\ \mu l} \times \frac{10^3\ \mu l}{1\ ml} \times \frac{mg\ Pb^{2+}}{10^3\ \mu g}, \quad \text{(A13)}$$

where 100 μl is the injection size and 250 ml is the volume of the lead sample solution.

$$\text{Wt. of } Pb_3O_4 \text{ in Sample, mg} = 1.875\ mg\ Pb^{2+} \times \frac{mmole\ Pb^{2+}}{207.21 mg\ Pb^{2+}} \times \frac{1\ mmole\ Pb_3O_4}{3\ mmole\ Pb^{2+}}$$

$$\times \frac{685.63\ mg\ Pb_3O_4}{mmole\ Pb_3O_4}, \quad \text{(A14)}$$

$$\%\ Pb_3O_4 = \frac{2.068\ mg\ Pb_3O_4}{25.00\ mg} \times 100 = 8.27\%\ Pb_3O_4, \quad \text{(A15)}$$

where 25.00 mg is the weight of the rubber sample dissolved in THF.

If the regression equation for the calibration curve has been calculated, the weight of Pb^{2+} in the injection can be calculated by inserting the peak area into Eq. (A12). The weight of Pb^{2+} in the sample can be calculated by inserting the weight of Pb^{2+} in the injection into Eq. (A10). The weight of Pb_3O_4 in the sample can be calculated by inserting the weight of Pb^{2+} in the sample into Eq. (A11). The percentage of Pb_3O_4 in the sample can be calculated by inserting the weight of Pb_3O_4 in the sample into Eq. (A9).

$$\text{Wt. of } Pb^{2+} \text{ in Injection, } \mu g = 6.2395E\text{-}06 \times 157898 - 2.3803E\text{-}01 = 0.747\ \mu g\ Pb^{2+} \quad \text{(A16)}$$

$$\text{Wt. of } Pb^{2+} \text{ in Sample, mg} = 0.747\ \mu g\ Pb^{2+} \times \frac{250\ ml}{100\ \mu l} \times \frac{10^3\ \mu l}{1\ ml} \times \frac{mg\ Pb^{2+}}{10^3\ \mu g}$$

$$= 1.868\ mg\ Pb^{2+} \quad \text{(A17)}$$

$$\text{Wt. of } Pb_3O_4 = 1.894\ mg \times \frac{1}{207.21} \times \frac{1}{3} \times \frac{685.63}{1} = 2.060\ mg\ Pb_3O_4 \quad \text{(A18)}$$

$$\% \, Pb_3O_4 = \frac{2.060 \text{ mg } Pb_3O_4}{25.00 \text{ mg}} \times 100 = 8.24 \, \% \, Pb_3O_4 \qquad \text{(A19)}$$

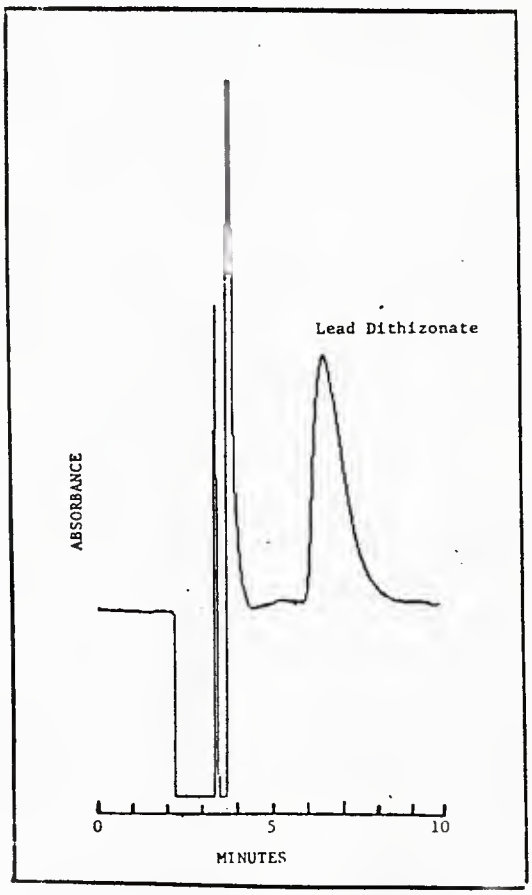

Fig. A5 - LC chromatogram of the lead recovered from a neoprene rubber sample

ESTIMATION OF CARBON BLACK CONTENT IN THE RUBBER SAMPLE

1. After the lead oxide has been removed from the nylon filter (by soaking in glacial acetic acid), the filter is carefully removed from the test tube and placed in a glass petri dish and in a warm oven (30 to 50°C) to remove excess moisture.

2. Once the surface moisture has been removed, the filter is dried at 100°C for 30 minutes.

3. The filter is cooled in a desiccator and weighed on a microbalance to the nearest 0.01 mg.

4. The weight gain of the filter (final weight minus the initial weight) is taken as an estimation of the carbon black content in the rubber sample.*

5. The carbon black content is reported as weight percent carbon using the following equation:

$$\% \text{ Carbon Black} = \frac{\text{Filter wt. gain, mg}}{\text{Sample wt., mg}} \times 100. \qquad \text{(A20)}$$

* NOTE: It should be emphasized that this gain in filter weight is taken to be an estimate of the carbon black content. It is recognized that this weight will include debris that has found its way into the rubber sample during compounding as well as any metal salts and gel residues that are not soluble in THF or glacial acetic acid.

Appendix B

NITRILE RUBBER ANALYTICAL PROCEDURES

INTRODUCTION

This section gives details of the quality control procedures developed for analyzing additives in uncured, compounded nitrile rubber. Reverse-phase HPLC measures the levels of TMTM, S_8, and ODPA. The zinc oxide (ZnO) content is measured by using complexation[8] chromatography, and an estimation of carbon black content is determined gravimetrically.

SAMPLE PREPARATION

1. Samples of uncured, compounded Nitrile BLT are stored in a 0°F freezer until analyzed.

2. Approximately 50 mg of rubber are cut from each sampling site on the frozen slab of rubber and diced into small (1 mm^3) pieces.

3. The diced rubber is placed in a desiccator for about 30 minutes to allow the rubber to come to room temperature and remove any absorbed moisture.

4. A 25 ±2-mg portion of the diced rubber is weighed to the nearest 0.01 mg on a microbalance and placed in a threaded test tube containing 6 ml of UV-grade THF. The tube is tightly sealed with a screw cap and gently agitated/rotated until the rubber has dissolved (about 30 minutes, depending upon the condition and state of cure of the elastomer).

5. The dissolved rubber sample is filtered into a 10.00-ml volumetric flask using a Millipore 47-mm stainless-steel filter and a dried, pre-weighed Rainin filter, 0.45-μm pore size. Prior to use, each filter is brought to constant weight by heating in an oven at 100°C for about 1 hr. After cooling, each filter is weighed to the nearest 0.01 mg on a microbalance and stored in a desiccator.

6. The solution in the volumetric flask is adjusted to 10.00 ml with UV-grade THF. The THF solution is now ready for LC additive analysis. The residue on the nylon filter contains zinc oxide, carbon black, and debris that have entered the sample during the compounding process. Additional processing of the residue on the filter is necessary to measure the carbon black and zinc oxide levels.

7. Uncured, compounded samples of nitrile may begin to cure at room temperature. Mistreatment will result in partially cured samples. An analysis of partially cured samples will produce poor data because they will not disperse completely in THF. When filtered (step 5, above), small, and irregularly shaped pieces of undissolved rubber will be found on the filter. In contrast, when an uncured sample is filtered, a smooth, even, velvet-like layer of carbon black and red lead is deposited on the filter. Suspect samples should be checked (prepare a new sample and attempt to disperse in THF) before proceeding with the HPLC analyses.

RECOVERY OF ZINC OXIDE FROM THE NYLON FILTER

1. To remove the ZnO collected on the filter during the filtration step, each filter is curled and placed into a test tube with 2.50 ml of reagent-grade glacial acetic acid.

2. The test tube is placed on a rotator and gently rotated for 1 hr. Distilled water is then added to cover the filter, and the solution is left on the rotator overnight.

3. The following day, the test tube is removed from the rotator and the acetic acid solution, which contains the dissolved lead, is quantitatively transferred to a 250.00-ml volumetric flask. The test tube and filter are washed with several portions of distilled water, and the washings are combined with the acetic acid in the 250.00-ml volumetric flask.

4. The nylon filter is soaked in about 10 ml of deionized water for about 10 min. This water is combined with the acetic acid solution in the volumetric flask. Washing of the filter is complete when you can no longer detect the odor of acetic acid in the test tube or filter.

5. The solution in the volumetric flask is diluted to 250.00 ml with deionized water and is now ready for LC analysis.

LIQUID CHROMATOGRAPHY ANALYSIS OF ORGANIC ADDITIVES

1. Optimized Operating Parameters

Column: Waters Z Module equipped with a μBondaPAK C_{18}, Radial-PAK Cartridge

Mobile Phase: 60% THF/H_2O [600 ml of filtered, UV-grade Burdick & Jackson THF to 400 ml of filtered deionized water (0.45-μm filter)].

Flow Rate: 2.00 ml/min.

Injection Size: 10-μl loop

Analysis Wavelength: 280 nm; Sensitivity = 0.02 AUFS (Optimum wavelength for sulfur is 254 nm; however 280 nm can be used to monitor all three additives if a dual wavelength detector is not available. In this report, the sulfur was monitored at 280 nm.)

A list of the chromatography and computer equipment used at NRL-USRD can be found in Table A1.

2. Detector Response Calibration

The UV detector response is calibrated for each additive by injecting standards of varying concentration and measuring the peak area for each injection. The concentration range for the standards should be varied from 10 to 200 ng for TMTM, from 20 to 700 ng for S_8, and from 100 to 3500 ng for ODPA. Stock solutions of standards should be prepared by accurately weighing material that has been dried in a desiccator for TMTM and ODPA (sulfur for

standard should be heated at 100°C for several hours) material and dissolving the standard material in UV-grade THF. As an example, a stock solution of TMTM and S_8 can be prepared by accurately weighing 10.00 mg and diluting to 100.00 ml in separate volumetric flasks. A stock solution of ODPA can be prepared in similar fashion by accurately weighing 50.00 mg and diluting to 100.00 ml. The concentration of the stock solutions for TMTM and S_8 is 100 ng/μl and for ODPA is 500 ng/μl. Three or, preferably, four dilutions should be made of each stock solution. Dilutions should cover the entire calibration range. Standards can be mixed in diluted solutions. Mixed standards are good for 1 day. A calibration curve should be prepared by plotting peak area (vertical axis) vs nanograms of standard injected (horizontal axis). When preparing the calibration curve, special attention should be given to the high concentration portion of the calibration curve where a nonlinear response may be encountered with some HPLC systems. If a nonlinear calibration curve is encountered, standard and sample solutions will have to be diluted to bring the calibration range into the linear response range of the detector. At the low end of the calibration curve, the curve should intersect the axes near zero area and zero concentration. If this is not observed, it may indicate that the standard solutions have begun to decompose or that the peak detection "window" of the computer software or the peak detection sensitivity (slope sensitivity) of the integrator is not properly set to detect each peak. This is particularly important in the case of TMTM (Fig. B4) which typically elutes in a very congested portion of the chromatogram. Figures B1, B2, and B3 show the calibration curves for each additive. Once established, the calibration curve for each additive is checked daily by injecting a mixed standards solution containing TMTM, S_8, and ODPA.

A regression equation describing the response of the detector over the concentration range of the calibration standards can also be calculated from the calibration data. The regression equation should be checked on a daily basis as described above. Calculation of a regression equation should not be used as a substitute for drawing a calibration curve.

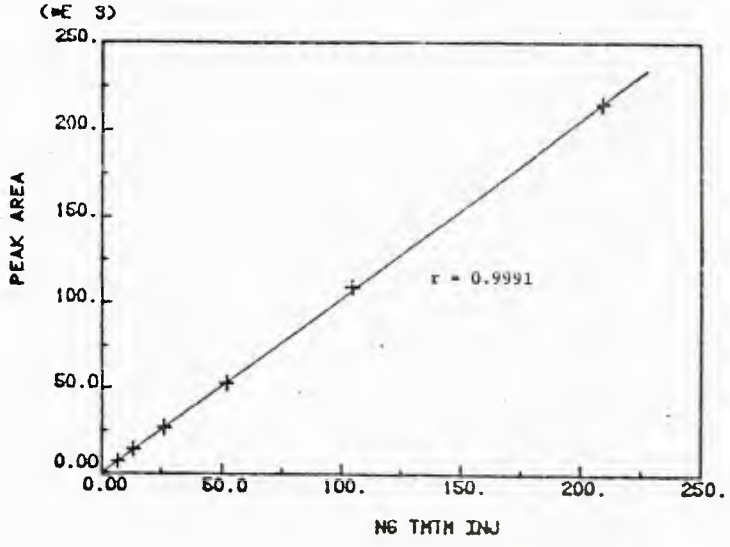

Fig. B1 - Calibration curve for TMTM

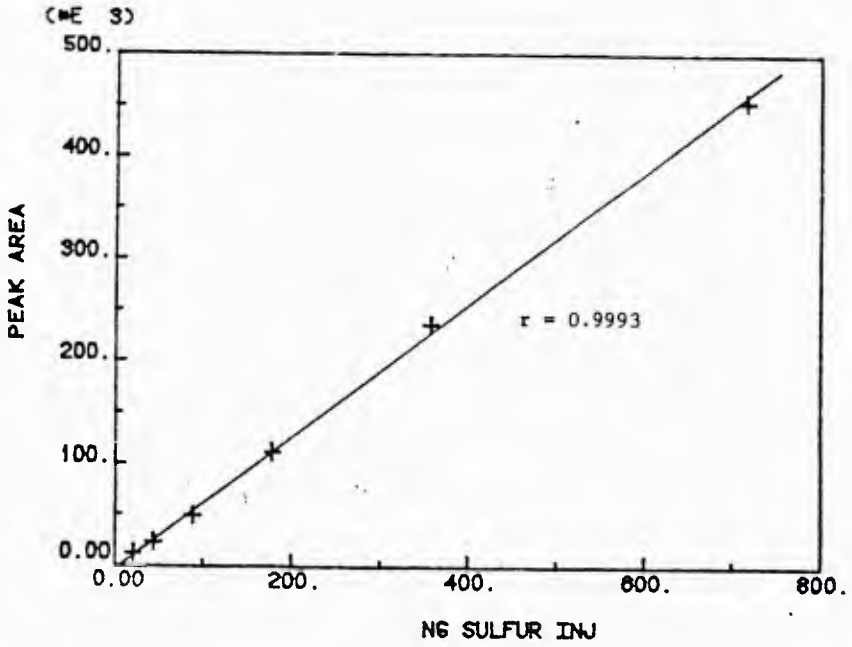

Fig. B2 - Calibration curve for sulfur at 280 nm

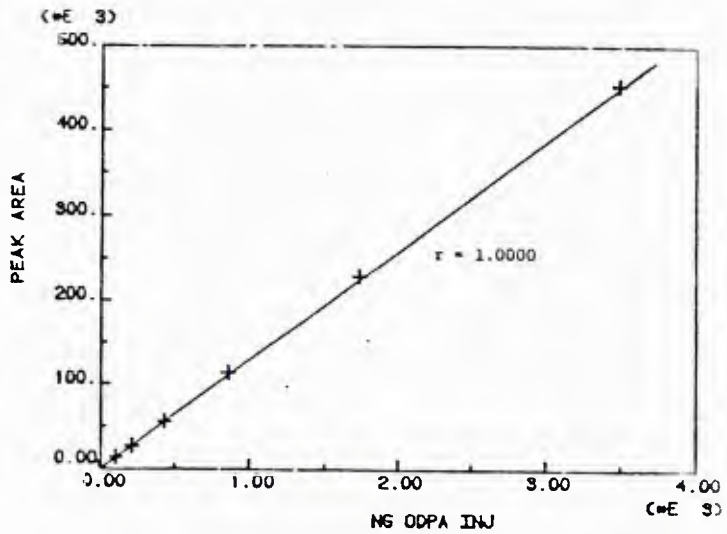

Fig. B3 - Calibration curve for ODPA

3. Chromatographing Mixed Standards and Rubber Solutions

NOTE: The procedure for generating the additive chromatograms will depend upon the LC equipment and data reduction facilities available. The procedure described below is for an automated LC system under computer control.

a. Optimum operating conditions are established on the LC by using the operating parameters listed in the previous section.

b. The autosampler vials are filled with the THF solutions of mixed standards and the dissolved, filtered rubber sample solutions.

c. A 10-μl portion of each solution is injected onto the column. At least three injections of each solution are chromatographed. TMTM, sulfur, and ODPA are monitored in each injection. Wash vials containing THF are placed between standard and sample vials (on the autosampler) to avoid cross contamination between solutions. Representative chromatograms of a mixed standard solution and a rubber solution are shown in Fig. B4.

d. When all of the standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to additive percentages.

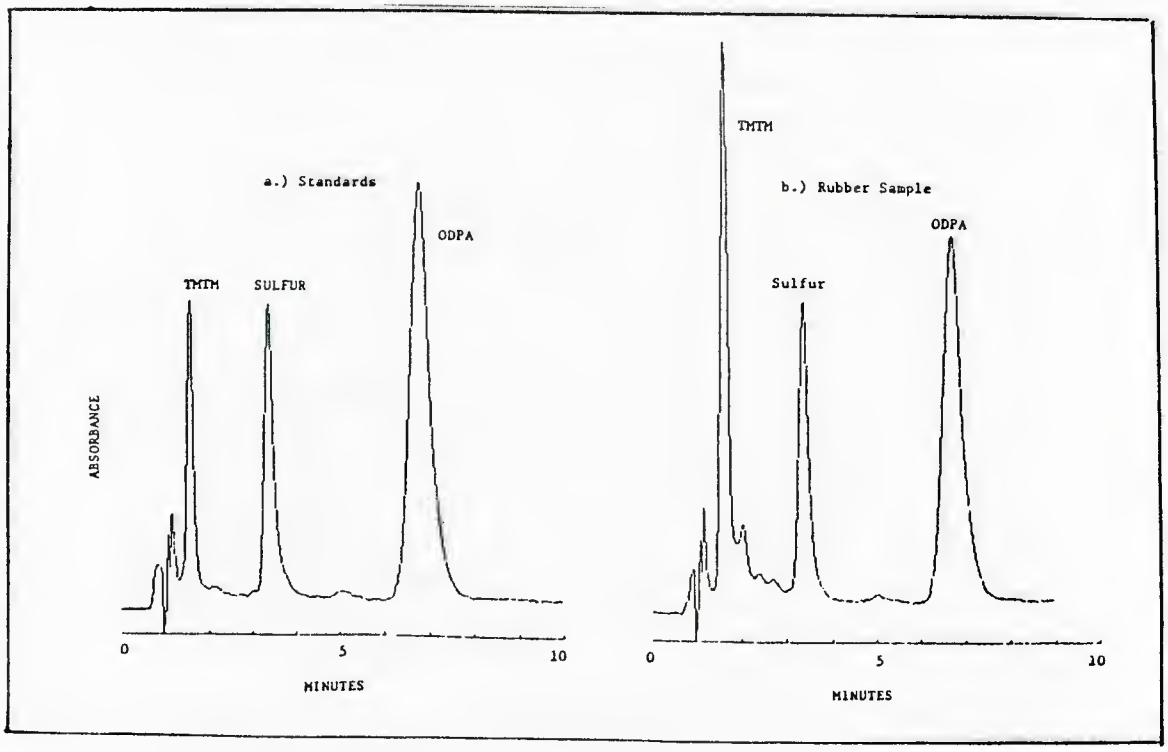

Fig. B4 - LC chromatogram of a mixed standard and a nitrile rubber sample

4. Data Reduction

The percentage of organic additive present in the rubber sample can be calculated using the following equation:

$$\% \text{ Additive} = \frac{\text{mg of additive present in the rubber sample}}{\text{sample weight, mg}} \times 100 , \qquad \text{(B1)}$$

where the mg of additive present in the rubber sample is determined experimentally using peak areas, the regression equation, and conversion factors shown below. Sample weight is the weight of the rubber sample initially dissolved in THF. An example of this type of calculation is shown in Appendix A.

$$\text{Wt. of Additive in Injection, ng} = \text{Slope of Regression Line} \times \text{Area Under Sample Cure} + \text{Intercept of Regression Line} \qquad \text{(B2)}$$

$$\text{Wt. of Additive in Sample, mg} = \text{Wt. of Additive in Injection, ng} \times \frac{\text{Dilution Volume (ml)}}{\text{Injection Volume } (\mu\text{l})}$$

$$\times \frac{10^3 \mu\text{l}}{1 \text{ ml}} \times \frac{1 \text{ mg}}{10^6 \text{ ng}} \qquad \text{(B3)}$$

LIQUID CHROMATOGRAPHY ANALYSIS OF ZINC OXIDE ((ZnO)

1. Optimized Operational Parameters

Column: Waters μBondaPAK C_{18}, 30 cm

Injection Size: 25-μl loop

Analysis Wavelength: 545 nm; Sensitivity = 0.05 or 0.10 AUFS

Mobile Phase: 70% Acetonitrile/30% Acetate Buffer pH 5.85/1.5 E-04M dithizone (procedure for preparation is given below)

Preparation of Acetate Buffer: 15.6-g anhydrous sodium acetate (25.9-g sodium acetate trihydrate) and 0.57-ml glacial acetic acid diluted to 1000.00 ml with dionized water

Purification of Dithizone: Dithizone is unstable and must be purified on a weekly basis. To purify, dissolve 1 g of dithizone in 50 to 75 ml of chloroform. Extract with four 100-ml portions of 0.2M NH_4OH. Filter the aqueous extracts into a separatory funnel. Acidify with 6M HCl until the solution becomes acidic to litmus paper, and extract prepicitate mixture with three 20-ml portions of $CHCl_3$. This stock solution of dithizone in chloroform should keep for several days if stored in the dark at 5 to 10°C.

Preparation of Mobile Phase: To prepare 1 liter of mobile phase, the chloroform is evaporated from several milliliters of the stock solution, and 35 mg of dried dithizone is weighed and dissolved in 700 ml of acetonitrile. The acetate buffer is added (300 ml) and the solution filtered (0.45 μm) and degassed. The mobile phase must be prepared fresh daily.

Flow Rate: 1.0 ml/min

Temperature: Ambient

Reactor Tubing: Reactor tubing is placed between the injector and column to assure complete metal-complex formation prior to entering the column. The reactor tubing is made by coiling 20 cm of 0.030-in. i.d. stainless-steel tubing.

2. Detector Response Calibration

The UV-detector response is calibrated daily by injecting standards of varying concentrations and measuring the peak area for each injection. Concentration of Zn^{2+} standard solutions should range from 5 to 400 ng injected. The stock solution of the standard should be prepared by accurately weighing dried ZnO and dissolving the ZnO in a suitable amount of glacial acetic acid such that the final concentration of acetic acid in the flask is 1%. For example, a stock solution containing 400 mg Zn^{2+}/liter may be prepared by dissolving 0.0498 g of ZnO in 1 ml of glacial acetic acid and diluting to 100.00 ml with HPLC-grade water. Three or, preferably, four dilutions of the stock solution using 1% acetic acid as the diluent should be prepared. A calibration curve should be prepared by plotting peak area (vertical axis) vs nanograms of standard injected (horizontal axis). When preparing the calibration curve, special attention should be given to the high concentration portion of the calibration curve where a nonlinear response may be encountered with some HPLC systems. If a nonlinear calibration curve is encountered, standard and sample solutions will have to be diluted to bring the calibration range into the linear response range of the detector. At the low end of the calibration curve, the curve should intersect the axes near zero area and zero concentration. If this is not observed, it may indicate that the mobile phase has begun to decompose or that the peak detection "window" of the computer software or the peak detection sensitivity (slope sensitivity) of the integrator was not properly set to detect the peak.

A regression equation describing the response of the detector over the concentration range of the calibration standards can also be calculated from the calibration data. The regression equation should be checked on a daily basis as described above. Calculation of a regression equation should not be used as a substitute for drawing a calibration curve.

3. Chromatographing Zinc Solutions

a. Optimum operating conditions are established on the LC by using the parameters in Section 1 of the Liquid Chromatography Analysis of Zinc Oxide.

b. The autosampler vials are filled with the dilute acetic acid solutions of zinc standards and zinc recovered from rubber.

c. A 25-μl portion of each zinc sample is injected. At least three injections are made on each solution. Wash vials of dilute acetic acid are placed between standard and sample vials (on the autosampler) to avoid cross contamination between samples. Representative chromatograms of a zinc standard solution and a rubber solution are shown in Fig. B5.

d. When all standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to zinc oxide percentages.

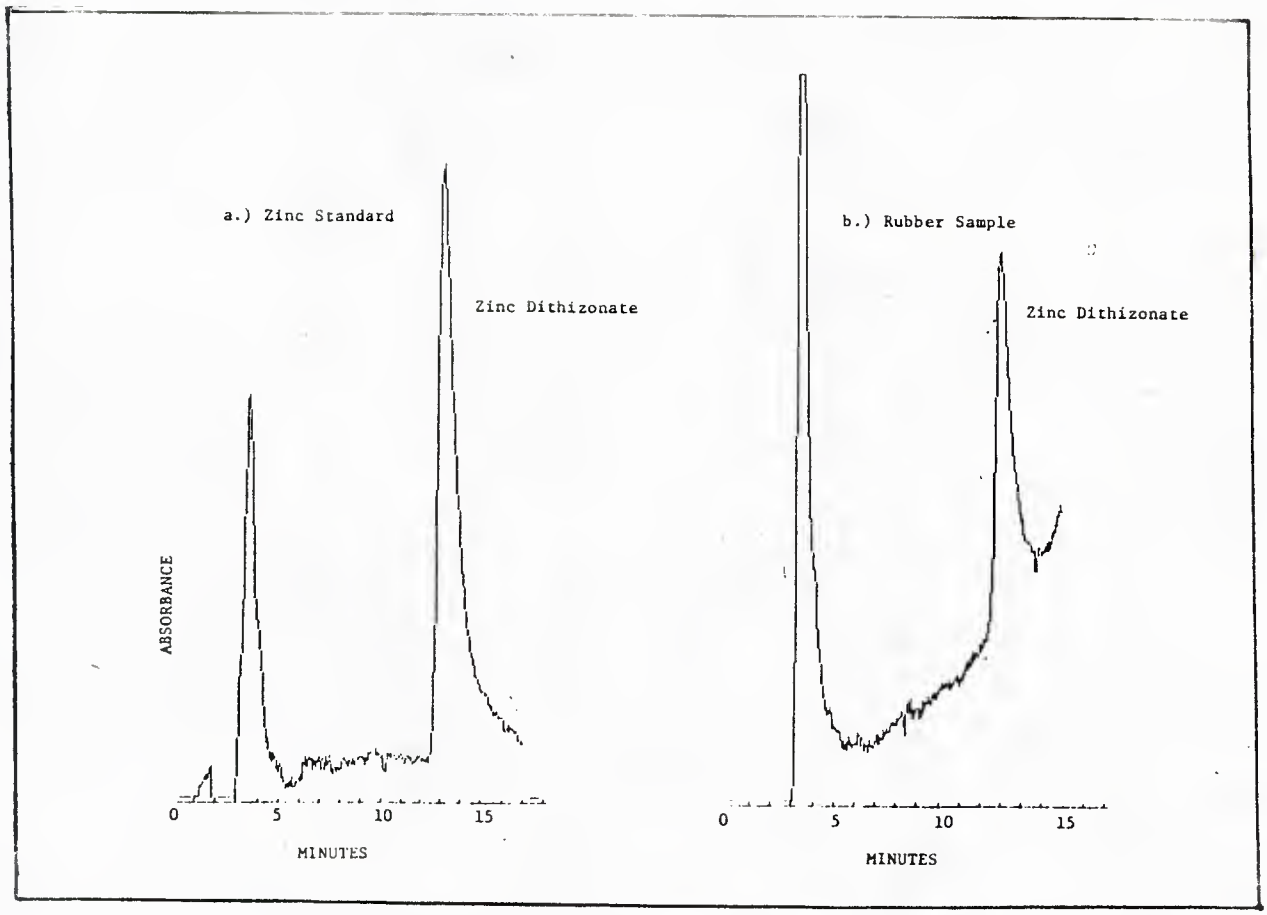

Fig. B5 - LC chromatogram of a mixed standard and a nitrile rubber sample

4. Data Reduction

The percentage of organic additive present in the rubber sample can be calculated using the following equation:

$$\% \text{ ZnO} = \frac{\text{mg of ZnO present in rubber sample}}{\text{sample wt., mg}} \times 100. \qquad \text{(B4)}$$

Where the milligrams of additive present in the rubber sample are determined experimentally using peak areas, the regression equation, and conversion

factors shown below and the sample weight are the initial weight of the rubber sample dissolved in THF.

$$\text{Wt. of } Zn^{2+} \text{ in Injection, ng} = \text{Slope of Regression Line} \times \text{Area Under Sample Curve} + \text{Intercept of Regression Line} \quad \text{(B5)}$$

$$\text{Wt. of } Zn^{2+} \text{ in Injection, mg} = \text{Wt. of } Zn^{2+} \text{ in Injection, ng} \times \frac{\text{Dilution Volume (ml)}}{\text{Injection Volume } (\mu l)} \times \frac{10^3 \mu l}{1 \text{ ml}} \times \frac{\text{mg } Zn^{2+}}{10^3 \mu g} \times \frac{\mu g}{10^3 \text{ ng}} \quad \text{(B6)}$$

To convert weight of Zn^{2+} in mg to ZnO, the following gravimetric factors are used.

$$\text{Wt. of ZnO, mg} = \text{Wt. of } Zn^{2+}\text{, mg} \times \frac{1 \text{ mmole } Zn^{2+}}{65.37 \text{ mg } Zn^{2+}} \times \frac{1 \text{ mmole ZnO}}{1 \text{ mmole } Zn^{2+}} \times \frac{81.36 \text{ mg ZnO}}{\text{mmol ZnO}} \quad \text{(B7)}$$

ESTIMATION OF CARBON BLACK CONTENT IN THE NITRILE RUBBER SAMPLE

Procedure 1: Gravimetric

1. After the zinc oxide has been removed from the nylon filter (by soaking in glacial acetic acid), the filter is carefully removed from the test tube and placed in a glass petri dish and in a warm oven (30 to 50°C) to remove excess moisture.

2. Once the surface moisture has been removed, the filter is dried at 100°C for 30 minutes.

3. The filter is cooled in a desiccator and weighed on a microbalance to the nearest 0.01 mg.

4. The weight gain of the filter (final weight minus the initial weight) is taken as a estimation of the carbon black content in the rubber sample.

5. The carbon black content is reported as weight percent carbon using the following equation:

$$\% \text{ Carbon Black} = \frac{\text{Filter weight gain, mg}}{\text{Sample weight, mg}} \times 100. \quad \text{(B8)}$$

Procedure 2: Thermogravimetric Analysis

The percentage of carbon black in a nitrile rubber can be determined more accurately by using thermogravimetric analysis (TGA). In TGA the weight loss of a sample is monitored while being subjected to a controlled temperature and environment. For a carbon black filled nitrile elastomer, the sample is heated in a nitrogen atmosphere to volatilize the plasticizers and pyrolytically decompose the rubber. At approximately 600°C the atmosphere is switched to air and the carbon black is combusted leaving an inert ash. From the thermogram obtained the percentage of carbon black in the elastomer can be calculated. Figure B6 shows the TG scan and the calculated carbon black content.

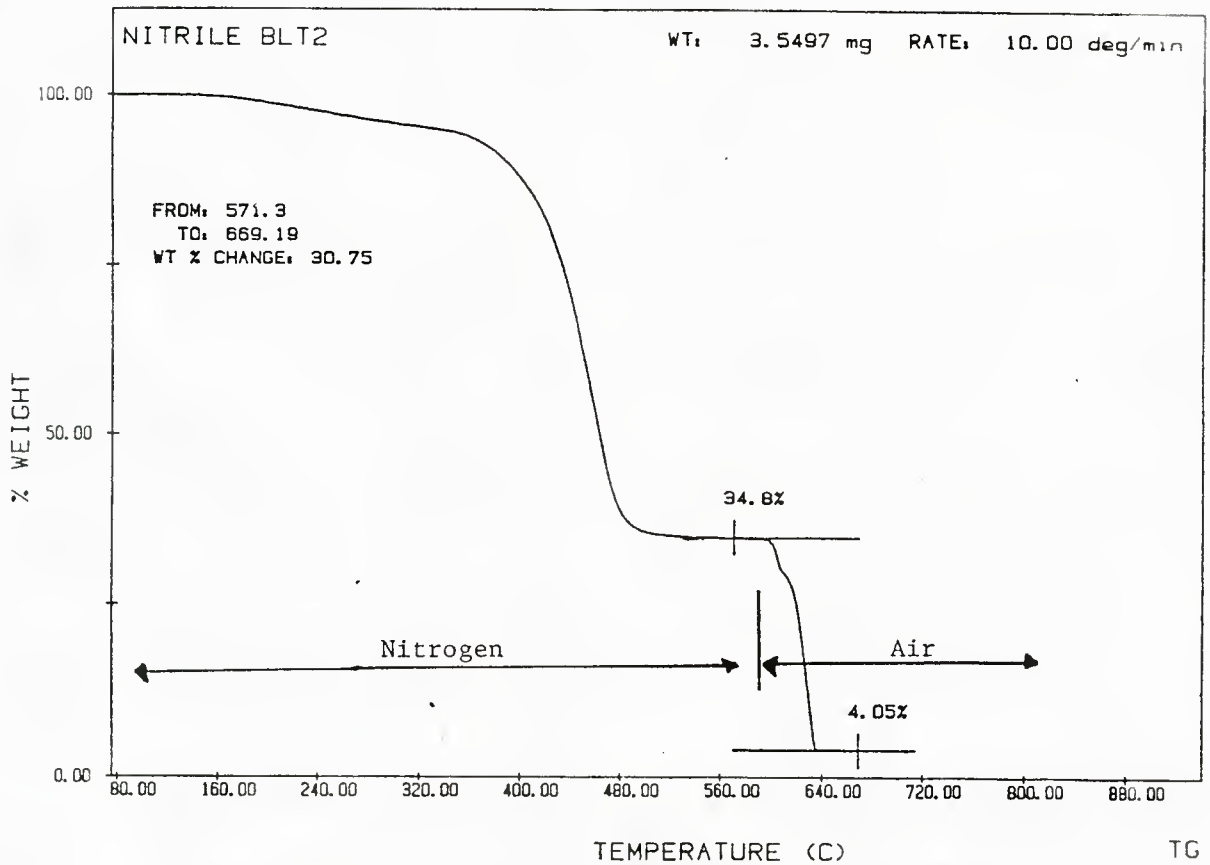

Fig. B6 - TG scan of a nitrile rubber sample showing the calculated carbon black content

ACRYLONITRILE CONTENT IN NITRILE RUBBER

Acrylonitrile content is most easily and accurately determined in the uncompounded nitrile rubber if a sample is available. If uncompounded rubber is not available, the compounded rubber must first be subjected to a thorough extraction. This should be done in an appropriately sized Soxhlet-style

extractor. Methanol and water in a 50-50 ratio by volume has been shown to adequately dissolve the interfering ODPA and TMTM without dissolving excessive polymer. Extraction for at least 4 hrs is required if the rubber pieces are cut into small (1-mm) cubes. With larger pieces, the extraction time must be longer.

The prescribed analysis measures only the total nitrogen content in the sample. Thus if a compounded sample is analyzed, the acrylonitrile content must be calculated from the presumed amount of additives in the rubber. This correction is done by calculating the weight of polymer in the sample that is weighed out for extraction, as follows:

$$\text{Wt. of polymer} = \text{wt. of sample} \times (100/150), \qquad \text{(B9)}$$

since 100 out of 150 parts are polymer. Obviously this introduces a significant imprecision into the analysis since there is little assurance that the additives have been added in the exact weights specified.

The analysis is performed by the Kjeldahl method as specified in ASTM D297, Method 54.* Permitted deviations from this procedure include the use of boric acid solution as the trapping medium with subsequent titration with sulfuric acid to a mixed bromcresol green-methyl red endpoint. The details of this latter method are given in ASTM D3533.**

The percent nitrogen calculated in either of the analytical procedures above must be converted into a percent acrylonitrile by multiplying by the gravimetric ratio, 3.788.

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* D297-81, Standard Methods for Rubber Products--Chemical Analysis," Annual Book of ASTM Standards, Part 37.

** D3533-76, "Standard Method of Testing Rubber--Nitrogen Content," Annual Book of ASTM Standards, Part 37.

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